

Full CI benchmark calculations on N₂, NO, and O₂: A comparison of methods for describing multiple bonds

Charles W. Bauschlicher, Jr. and Stephen R. Langhoff
NASA Ames Research Center, Moffett Field, California 94035

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Full configuration interaction (CI) calculations on the ground states of N₂, NO, and O₂ using a DZP Gaussian basis are compared with single-reference SDCl and coupled pair approaches (CPF), as well as with CASSCF multireference CI approaches. The CASSCF/MRCI technique is found to describe multiple bonds as well as single bonds. Although the coupled pair functional approach gave chemical accuracy (1 kcal/mol) for bonds involving hydrogen, larger errors occur in the CPF approach for the multiple bonded systems considered here. CI studies on the ¹Σ_g⁺ state of N₂, including all single, double, triple, and quadruple excitations show that triple excitations are very important for the multiple bond case, and accounts for most of the deficiency in the coupled pair functional methods.

I. INTRODUCTION

Full configuration interaction (FCI) calculations have been instrumental in benchmarking approximate solutions to the electron correlation problem. Recent FCI calculations have delineated the limitations of existing CI methods in accounting for the correlation contribution to electron affinities,^{1,2} *T_e* values,³⁻⁵ barriers to chemical reactions,⁶ the energy associated with stretching bonds,^{2,3,5,7} and molecular properties.^{7,8} In all of these applications the complete active space self-consistent-field (CASSCF)⁹ calculation followed by a multireference singles and doubles excitation CI (MRCI) treatment gave the best agreement with the FCI results. Single-reference SDCl calculations based upon SCF orbitals yielded rather poor results in this series of benchmark calculations. However, improved results were obtained when corrections for unlinked higher excitations were included either by the Davidson correction¹⁰ or with coupled pair functional (CPF) methods.^{11,12} For breaking single bonds with hydrogen, the CPF approach gave excellent agreement with the FCI; for example, the *r_e*, *ω_e*, *D_e*, and dipole moment function for the X²Π state of OH are all in excellent agreement⁷ with the FCI and CASSCF/MRCI results.

In this work we extend our FCI studies to N₂, NO, and O₂ that have electron dense multiple bonds. We compare the FCI energies with those obtained from approximate methods of including electron correlation for internuclear distances near *r_e*, as well as at larger *r* values to illustrate not only how well different methods do for the spectroscopic parameters (*r_e*, *ω_e*, *D_e*), but on the energetics of the bond breaking process.

II. METHODS

The [4s2p] Dunning contractions¹³ of the Huzinaga¹⁴ (9s5p) primitive sets are used for nitrogen and oxygen. A set of *d* polarization functions is added (3s component excluded) with exponents of 0.8 for nitrogen and 0.9 for oxygen. Since these calculations may be used to benchmark other methods, these (9s5p1d)/[4s2p1d] basis sets are given explicitly in Table I.

The single-reference correlation methods are based on the SCF occupations for the ground states:

$$\text{N}_2: {}^1\Sigma_g^+ 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4, \quad (1)$$

$$\text{NO}: {}^2\Pi 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1, \quad (2)$$

$$\text{O}_2: {}^3\Sigma_g^- 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2. \quad (3)$$

The calculations are performed with both symmetry and equivalence restrictions. Since the SCF configurations do not dissociate correctly to neutral atoms, the dissociation energy was computed using a supermolecule approach based upon the occupations

$$\text{N}_2: {}^7\Sigma_u^+ 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 3\sigma_u^1 1\pi_u^2 1\pi_g^2, \quad (4)$$

$$\text{NO}: {}^6\Pi 1\sigma^2 2\sigma^3 3\sigma^2 4\sigma^2 5\sigma^1 6\sigma^1 1\pi^3 2\pi^2, \quad (5)$$

$$\text{O}_2: {}^5\Delta_g 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 3\sigma_u^1 1\pi_{ux}^1 1\pi_{uy}^1 1\pi_{gx}^1 1\pi_{gy}^1. \quad (6)$$

For O₂ the equivalence restriction was eliminated so that the wave function is described by a single configuration in *D_{2h}* symmetry. Since the wave function is symmetry broken, it is actually a linear combination of ⁵Δ_g and ⁵Σ_g⁺, which are degenerate at infinite separation. The supermolecule calculation for these occupations is also used to compute *D_e* for the SDCl, CPF, and MCPF treatments. In the FCI calculations, the energy for the separated systems is taken as the sum of the atomic energies.

The MRCI treatments are based on CASSCF wave functions in which the 2*p* orbitals and electrons are active. As for the SCF calculations, symmetry and equivalence restrictions are imposed. Since the CASSCF wave function correctly dissociates to ground state atoms, the same configuration expansion was used at all geometries, i.e., *D_e* is computed from a supermolecule calculation.

Since inclusion of 2*s* correlation results in prohibitively long FCI expansions, only the 2*p* electrons were correlated. Previous work¹⁵ has shown that when only the *np* electrons are correlated, it is important to localize the *ns* orbital so that it is not changing in an arbitrary manner with bond distance. For the CASSCF wave functions, the 2*s* and 2*p* orbitals are uniquely defined since they are inequivalent. For the SCF treatment, we localize the 2*s* orbital by performing a CASSCF calculation at each geometry, and then freezing

TABLE I. Basis sets.

N (9s5p1d)/[4s2p1d]	
s	p
5909.440(0.002 004)	26.7860(0.018 257)
887.4510(0.015 310)	5.9564(0.116 407)
204.7490(0.074 293)	1.7074(0.390 111)
59.8376(0.253 364)	0.5314(0.637 221)
19.9981(0.600 576)	0.1654(1.000 000)
2.6860(0.245 111)	
7.1927(1.000 000)	
0.7000(1.000 000)	d
0.2133(1.000 000)	0.80(1.000 000)
O (9s5p1d)/[4s2p1d]	
s	p
7816.54(0.002 031)	35.1832(0.019 580)
1175.82(0.015 436)	7.9040(0.124 189)
273.188(0.073 771)	2.3051(0.394 727)
81.1696(0.247 606)	0.7171(0.627 375)
27.1836(0.611 832)	0.2137(1.000 000)
3.4136(0.241 205)	
9.5322(1.000 000)	d
0.9398(1.000 000)	0.9000(1.000 000)
0.2846(1.000 000)	

the 1s- and 2s-like orbitals in this form. The remaining orbitals are then optimized with this constraint in an SCF calculation. At large internuclear separations, the 2s and 2p orbitals are inequivalent so that this procedure is identical to a fully variational SCF treatment. Since the SCF spectroscopic parameters are nearly unchanged by replacing the fully variational 1s and 2s orbitals with CASSCF core orbitals, the localization of the 2s does not significantly degrade the single configuration description of the wave function. Hence, these orbitals were used in all of the single-reference calculations. For N₂, we also used the CASSCF orbitals as the basis for the single-reference approaches, to determine the importance of the SCF optimization for the valence orbitals. As we show later, replacing all of the SCF orbitals by CASSCF orbitals has a much larger deleterious effect than only replacing the inner 1s and 2s orbitals.

The single-reference methods considered include singles and doubles CI (with and without a Davidson correction—denoted +Q), the coupled pair functional method (CPF) of Ahlrichs *et al.*¹¹ (Chong–Langhoff¹² implementation) and the modified CPF (denoted MCPF) of Chong and Langhoff.¹² In addition, for the X¹Σ_g⁺ state of N₂, we added to the SDCI wave function all triple excitations (denoted SDTCI), all quadruple excitations (denoted SDQCI), and both sets (denoted SDTQCI).

In addition to the single-reference methods, we have carried out singles and doubles MRCI calculations with the reference space comprised of all CSFs in the CASSCF wave function, that is a full second-order CI. To the MRCI energies we have also added the multireference analog of the Davidson correction, which can be written as ΔE_{SD}(1 - Σ_R C_R²), where ΔE_{SD} is the difference between the energy of the reference CSFs and the MRCI, and the C_R are the coefficients of the reference configurations in the MRCI wave function.

The FCI calculations were performed on the NAS CRAY 2 using a modified version of the Knowles and

TABLE II. Comparison of N₂ spectroscopic constants with level of correlation treatment.

	r _e (a ₀)	ω _e (cm ⁻¹)	D _e (eV)
FCI	2.123	2333	8.750
SCF(no constraints)-FCI	-0.078	364	-4.131
SCF(CASSCF core)-FCI	-0.078	366	-4.137
1-REF(CASSCF orbitals)-FCI	-0.080	377	-4.195
CASSCF-FCI	-0.004	-1	-0.416
SCF(CASSCF core) orbitals			
SDCI-FCI	-0.021	103	-0.452
SDCI + Q-FCI	-0.008	40	-0.137
MCPF-FCI	-0.009	37	-0.194
CPF-FCI	-0.011	49	-0.224
SDTCI-FCI	-0.016	78	-0.288
SDTQCI-FCI	-0.002	10	-0.018
SDQCI-FCI	-0.007	28	-0.164
CASSCF orbitals			
SDCI-FCI	-0.023	113	-0.481
SDCI + Q-FCI	-0.011	53	-0.177
MCPF-FCI	-0.011	50	-0.231
CPF-FCI	-0.013	62	-0.261
MRCI-FCI	0.000	1	-0.007
MRCI + Q-FCI	0.000	0	+0.016

Handy code,¹⁶ which has been interfaced with the MOLECULE-SWEDEN program system.^{17,18} All other calculations were performed using the MOLECULE-SWEDEN system on the NASA Ames CRAY XMP 48. The FCI calculations on the ³Σ_g⁻ state of O₂ required about 3430 s per iteration or about 10 h of CRAY 2 time per geometry. The FCI calculations consisted of 21 382 384 determinants and 171 028 000 intermediate states. Most of the computational time is spent performing matrix multiplies, which executes between 285–420 MFLOPS on one processor of the CRAY 2 depending on system load, i.e., the degree of bank conflicts with the other processors.

III. RESULTS AND DISCUSSION

The spectroscopic parameters at the FCI level using the DZP basis are given for N₂ (X¹Σ_g⁺), NO (X²Π), and O₂ (X³Σ_g⁻) in Tables II to IV, respectively. The spectroscopic parameters r_e and ω_e are computed using three points with 0.05 a₀ separation fit to a second-degree polynomial in 1/R. Spectroscopic parameters for all approximate treatments are given relative to the FCI in Tables II–IV. The relative accu-

TABLE III. Comparison of NO spectroscopic constants with level of correlation treatment.

	r _e (a ₀)	ω _e (cm ⁻¹)	D _e (eV)
FCI	2.220	1914	5.754
SCF(no constraints)-FCI	-0.090	332	-3.752
SCF(CASSCF core)-FCI	-0.091	336	-3.762
CASSCF-FCI	0.003	-23	-0.854
SCF(CASSCF core) orbitals			
SDCI-FCI	-0.027	104	-0.458
SDCI + Q-FCI	-0.009	27	-0.130
MCPF-FCI	-0.009	21	-0.171
CPF-FCI	-0.011	30	-0.200
CASSCF orbitals			
MRCI-FCI	-0.001	0	-0.018
MRCI + Q-FCI	0.000	0	+0.023

TABLE IV. Comparison of O₂ spectroscopic constants with level of correlation treatment.

	r_e (a_0)	ω_e (cm^{-1})	D_e (eV)
FCI	2.318	1600	4.637
SCF(no constraints)-FCI	-0.118	407	-3.665
SCF(CASSCF core)-FCI	-0.119	409	-3.666
CASSCF-FCI	0.004	-40	-0.958
	SCF(CASSCF core) orbitals		
SDCI-FCI	-0.036	109	-0.465
SDCI + Q-FCI	-0.014	46	-0.135
MCPF-FCI	-0.013	37	-0.150
CPF-FCI	-0.017	50	-0.189
	CASSCF orbitals		
MRCI-FCI	0.000	0	-0.024
MRCI + Q-FCI	0.001	1	+0.040

accuracy of the approximate methods is similar for all three systems. Sizable errors occur in all of the spectroscopic parameters at the SCF level. For example, the error in r_e increases from 0.078 a_0 in N₂ to 0.118 a_0 in O₂. These errors are two orders of magnitude larger than the difference between the fully variational SCF and the SCF with a frozen CASSCF core. The errors in ω_e are also large at the SCF level, and the SCF recovers at most 50% of the FCI D_e . In contrast, the CASSCF treatment has only small errors in r_e and ω_e , and recovers nearly 80% of the FCI D_e in all cases. Clearly, the CASSCF wave function supplies a much better starting description of these systems than does SCF.

The inclusion of electron correlation with the SDCI treatment reduces the error in r_e by about a factor of 3, but the error still increases from N₂ to O₂. The error in ω_e and D_e at the SDCI level is still large and is about the same for all three systems. The spectroscopic parameters are improved if a correction is included for higher excitations. The SDCI + Q, CPF, and MCPF give comparable accuracy. The MCPF method is slightly better than CPF, and SDCI + Q gives the best D_e values. However, none of the single-reference approaches give D_e values within 1 kcal/mol of the FCI values.

The r_e and ω_e values from the CASSCF/MRCI treatment agree with the FCI results to within the accuracy of the fit, and the D_e has less than 0.6 kcal/mol error. While the inclusion of the Davidson correction improves the single-reference results, it has almost no effect on the MRCI r_e or

ω_e . However, the multireference Davidson correction results in an overestimation of D_e by as much as 0.04 eV for O₂. Hence, it appears that the multireference Davidson correction is overcounting the effect of higher excitations to some extent.

For N₂ several additional calibration calculations were performed. First, we tested the sensitivity of the single-reference methods to the molecular orbital basis by performing the SDCI and CPF calculations using the CASSCF orbitals. At both the single-reference and correlated level, the errors in the calculated spectroscopic constants (r_e , ω_e , D_e) are slightly larger when the CASSCF orbitals were used. This suggests that the SCF orbitals are best when the system is well described by a single configuration. Note, however, that replacing only the 1s and 2s orbitals by CASSCF orbitals has little effect on the computed energies.

The error in the SDCI, SDCI + Q, and CPF based methods for these multiple bonded systems are much larger than comparable calculations on first-row hydride systems. For example for the X²Π state of OH,⁷ the errors in SDCI treatment are -0.008 a_0 , 58 cm^{-1} , and -0.110 eV for r_e , ω_e , and D_e , respectively. The inclusion of more extensive correlation in the MCPF(CPF) approach significantly reduces these errors to -0.001 (-0.001) a_0 , 1.8(5.2) cm^{-1} , and -0.030 (-0.034) eV. Hence, the errors for the multiple-bond case are substantially greater than for OH. To investigate the origin of the larger errors, we carried out additional CI calculations for N₂ that selectively add to the SDCI wave function all triple, all quadruple and both classes of excitations. The SDQCI results show that the +Q correction overestimates the quadruples contribution to D_e by about 0.03 eV, which is about the same amount that MCPF underestimates D_e . However, both SDCI + Q and CPF account for most of the effect of the quadruple excitations. The importance of the triple excitations, as measured by either the difference between the SDCI and SDTCI or between SDQCI and SDTQCI, indicate that the largest error in the SDCI + Q, MCPF, and CPF calculations is the neglect of triple excitations. Since the triples contribute about 0.15 eV to D_e , it is impossible to achieve chemical accuracy without accounting for them.

The total energies for all levels of treatment for N₂, NO, and O₂ can be constructed from Tables V-VII, respectively. While the MCPF D_e for N₂ is low by 0.19 eV, this calculation accounts for 96.4% of the valence correlation energy

TABLE V. Summary of total energies, in E_H , for O₂. For the FCI, SCF, and CASSCF the total energy is given, while for the remaining calculations the difference with the FCI is reported.

	2.25	2.30	2.35	100.0
SCF ^a	-149.635 018	-149.630 930	-149.624 734	-149.601 092
CASSCF	-149.731 897	-149.733 778	-149.733 689	-149.598 800
FCI	-149.875 147	-149.876 947	-149.876 694	-149.706 685
SDCI-FCI	+0.018 575	+0.020 035	+0.021 576	+0.002 965
SDCI + Q-FCI	+0.003 948	+0.004 500	+0.005 094	-0.000 316
MCPF-FCI	+0.005 455	+0.005 980	+0.006 529	+0.000 584
CPF-FCI	+0.006 561	+0.007 222	+0.007 922	+0.000 415
MRCI-FCI	+0.004 073	+0.004 105	+0.004 132	+0.003 219
MRCI + Q-FCI	-0.001 782	-0.001 811	-0.001 836	-0.000 361

^aThe SCF has the 1s- and 2s-like orbitals defined by the CASSCF calculation.

TABLE VI. Summary of the relative shape of the potential curves for N₂. At 50.0 a₀ the FCI total energy is given, while at all other geometries the difference with 50.0 a₀ is given. For all other levels of treatment the potential is reported as the difference with the FCI.

	2.05	2.10	2.15	
FCI	-0.317 389	-0.321 123	-0.320 975	
SCF ^a -FCI	0.147 887	0.154 396	0.161 053	
CASSCF-FCI	0.014 879	0.015 163	0.015 410	
	SCF with CASSCF core orbitals			
SDCI-FCI	0.014 677	0.016 189	0.017 817	
SDCI + Q-FCI	0.004 262	0.004 800	0.005 389	
MCPF-FCI	0.006 267	0.006 878	0.007 522	
CPF-FCI	0.007 223	0.007 968	0.008 765	
SDTCI-FCI	0.009 135	0.010 206	0.011 375	
SDTQCI-FCI	0.000 508	0.000 611	0.000 732	
	CASSCF orbitals			
SDCI-FCI	0.015 620	0.017 258	0.019 024	
SDCI + Q-FCI	0.005 486	0.006 200	0.006 982	
MCPF-FCI	0.007 396	0.008 171	0.008 997	
CPF-FCI	0.008 391	0.009 306	0.010 289	
MRCI-FCI	0.000 220	0.000 229	0.000 241	
MRCI + Q-FCI	0.000 020	0.000 010	0.000 003	
	2.50	3.00	4.00	50.0
FCI	-0.257 799	-0.128 007	-0.012 695	-108.829 519
SCF ^a -FCI	0.211 965	0.298 862	0.518 224	+0.040 735
CASSCF-FCI	0.016 342	0.016 383	0.007 361	+0.040 735
	SCF with CASSCF core orbitals			
SDCI-FCI	0.032 921	0.067 755	0.180 736	+0.000 487
SDCI + Q-FCI	0.011 136	0.022 932	0.011 809	-0.000 121
MCPF-FCI	0.012 628	0.010 896	... ^b	+0.000 112
CPF-FCI	0.015 645	0.017 624	... ^b	+0.000 073
SDTCI-FCI	0.022 834	0.051 695	0.150 013	+0.000 315
SDTQCI-FCI	0.002 297	0.007 984	0.025 884	+0.000 003
	CASSCF orbitals			
SDCI-FCI	0.035 378	0.072 590	0.189 708	+0.000 487
SDCI + Q-FCI	0.014 469	0.028 585	-0.005 443	-0.000 121
MCPF-FCI	0.015 722	0.014 529	... ^b	+0.000 112
CPF-FCI	0.018 846	... ^b	... ^b	+0.000 073
MRCI-FCI	0.000 276	0.000 296	0.000 162	+0.000 487
MRCI + Q-FCI	-0.000 081	-0.000 220	-0.000 152	-0.000 121

^a The SCF has the 1s- and 2s-like orbitals defined by the CASSCF calculation.

^b It was not possible to achieve convergence.

obtainable in this one-particle basis at $R = 2.1 a_0$, or more than 5 eV of the correlation energy. Hence, the magnitude of the correlation energy in these multiple-bonded systems is so large that even a few percent error becomes a significant error in the total energy.

While the total energies are important for benchmarking other methods, more insight into the accuracy of different correlation methods is obtained by comparing the computed potentials to the FCI. To facilitate this comparison all the potentials are shifted to bring the energies at 50 a₀ into coincidence, and the difference between each level of theory and the FCI is reported. These results for N₂ and NO are summarized in Tables VI and VII. These results are also displayed graphically for N₂ in Fig. 1. Since the SCF does not correctly dissociate, we have used the occupations in Eqs. (4) and (5) for infinite separation. The SCF potential at 4.00 a₀ for N₂ is in error by more than 14 eV relative to the FCI, a factor of 3.4 larger error than at r_e . For NO, which has a bond order of 2.5 compared to 3 for N₂, the SCF potential at 4.4 a₀ is in error by 6.8 eV, which is a 3 eV larger error than at r_e . Considering the magnitude of the errors in the SCF, it is not surprising that the single-reference approaches

have larger errors at longer bond lengths. In fact at the longer bond lengths it was not always possible to obtain a converged CPF or MCPF solution; for NO at 4.4 a₀ the reference configuration accounts for only 6% for the SDCI wave function. For NO even at 3.30 a₀, the quality of the reference is so poor that the Davidson correction overshoots the FCI energy. The SDTQCI results for N₂ are better than the MCPF or CPF results, however even this treatment breaks down at large bond distances (see Fig. 1), since the correct description of two separated nitrogen atoms requires sixfold excitations. If the CASSCF orbitals are substituted for the SCF orbitals, the breakdown of the MCPF and CPF treatments occurs at even shorter bond lengths. This is further support for obtaining the best single-reference description for the CPF or MCPF approaches.

Unlike the SCF, the CASSCF approach yields much more uniform accuracy with increasing bond length. For N₂ the maximum error in the CASSCF is only 0.45 eV, while it is larger (0.86 eV) for NO, but it is still very small compared to the SCF. Given the accuracy and consistency of the CASSCF treatment, it is not surprising that the error at the MRCI level is small and nearly constant with bond length.

TABLE VII. Summary of the relative shape of the potential curves for NO. At 50.0 a_0 the FCI total energy is given, while at all other geometries the difference with 50.0 a_0 is given. For all other levels of treatment the potential is reported as the difference with the FCI.

	2.15	2.20	2.25
FCI	-0.208 732	-0.211 223	-0.210 958
SCF ^a -FCI	0.135 819	0.141 379	0.147 003
CASSCF-FCI	0.031 583	0.031 439	0.031 253
SDCI-FCI	0.015 185	0.016 614	0.018 139
SDCI + Q-FCI	0.004 210	0.004 647	0.005 103
MCPF-FCI	0.005 665	0.006 122	0.006 578
CPF-FCI	0.006 597	0.007 170	0.007 750
MRCI-FCI	0.000 646	0.000 655	0.000 663
MRCI + Q-FCI	-0.000 835	-0.000 852	-0.000 867
	3.30	4.40	50.0
FCI	-0.053 141	-0.004 628	-129.268 102
SCF ^a -FCI	0.245 321	0.250 255	+0.074 310
CASSCF-FCI	0.020 075	0.003 629	+0.074 310
SDCI-FCI	0.070 476	0.077 502	+0.001 532
SDCI + Q-FCI	-0.062 803	... ^b	-0.000 289
MCPF-FCI	0.019 370	... ^c	+0.000 228
CPF-FCI	... ^c	... ^c	+0.000 250
MRCI-FCI	0.000 584	0.000 139	+0.001 529
MRCI + Q-FCI	-0.000 698	-0.000 101	-0.000 292

^a The SCF has the 1s- and 2s-like orbitals defined by the CASSCF calculation.

^b The reference is only 0.6% of the wave function.

^c It was not possible to achieve convergence.

Therefore, not only does the CASSCF/MRCI supply a good description of the potential near r_e , it describes the whole potential equally well, even the region where three bonds are being broken. These observations are dramatically illustrated for N₂ in Fig. 1, where only the MRCI and MRCI + Q potentials are observed to be in quantitative agreement with the FCI as the bonds are stretched.

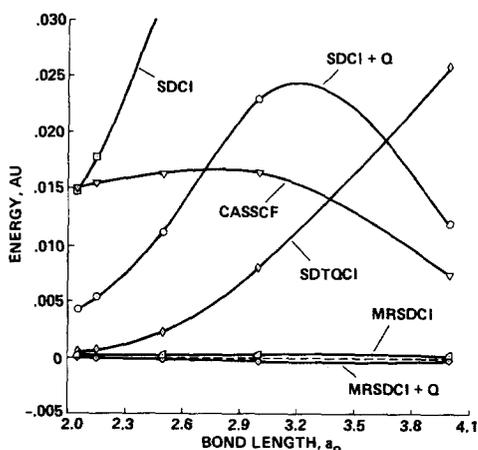


FIG. 1. Comparison of the energy differences between the FCI potential and selected approximate methods of including electron correlation as a function of bond distance for the $X^1\Sigma_g^+$ state of N₂.

IV. CONCLUSIONS

The spectroscopic parameters computed at the single-reference SDCI level for the ground states of N₂, NO, and O₂ differ significantly from the FCI results, because the SCF is a poor zeroth-order description of these electron dense multiple-bonded systems. Inclusion of quadruple excitations either explicitly (SDQCI calculations) or approximately with the SDCI + Q, MCPF, and CPF treatments, gives substantially reduced errors. The SDTQCI calculations for N₂ yield spectroscopic parameters in good agreement with the FCI, indicating that the main deficiency of the CPF approach is the neglect of triple excitations, which are quite important for these systems. The CASSCF calculations yield a much improved potential, better even than SDCI in many respects. The addition of more extensive correlation to the CASSCF zeroth-order reference yields spectroscopic parameters in near perfect agreement with the FCI. However, the addition of a multireference Davidson correction results in energies below the FCI and a slight overestimation of D_e . Although these multiple-bonded systems are more challenging computationally than, for example, the hydrides, the CASSCF/MRCI approach provides a quantitative treatment of the n -particle problem.

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- ¹C. W. Bauschlicher, S. R. Langhoff, H. Partridge, and P. R. Taylor, *J. Chem. Phys.* **85**, 3407 (1986).
- ²C. W. Bauschlicher and P. R. Taylor, *J. Chem. Phys.* **85**, 2779 (1986).
- ³C. W. Bauschlicher, S. R. Langhoff, P. R. Taylor, N. C. Handy, and P. J. Knowles, *J. Chem. Phys.* **85**, 1469 (1986).
- ⁴C. W. Bauschlicher and P. R. Taylor, *J. Chem. Phys.* **85**, 6510 (1986).
- ⁵C. W. Bauschlicher and P. R. Taylor, *J. Chem. Phys.* **86**, 1420 (1987).
- ⁶C. W. Bauschlicher and P. R. Taylor, *J. Chem. Phys.* **86**, 858 (1987).
- ⁷S. R. Langhoff, C. W. Bauschlicher, and P. R. Taylor (in press).
- ⁸C. W. Bauschlicher and P. R. Taylor, *Theor. Chim. Acta* (in press).
- ⁹E. M. Siegbahn, A. Heiberg, B. O. Roos, and B. Levy, *Phys. Scr.* **21**, 323 (1980); B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, *Chem. Phys.* **48**, 157 (1980); B. O. Roos, *Int. J. Quantum Chem. Symp.* **14**, 175 (1980).
- ¹⁰S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.* **8**, 61 (1974).
- ¹¹R. Ahlrichs, P. Scharf, and C. Ehrhardt, *J. Chem. Phys.* **82**, 890 (1985).
- ¹²D. P. Chong and S. R. Langhoff, *J. Chem. Phys.* **84**, 5606 (1986).
- ¹³T. H. Dunning, *J. Chem. Phys.* **53**, 2823 (1970).
- ¹⁴S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
- ¹⁵L. G. M. Pettersson, S. R. Langhoff, and D. P. Chong, *J. Chem. Phys.* **85**, 2836 (1986); see also P. Scharf and R. Ahlrichs, *Chem. Phys.* **100**, 237 (1985).
- ¹⁶P. J. Knowles and N. C. Handy, *Chem. Phys. Lett.* **111**, 315 (1984); see also P. E. M. Siegbahn, *ibid.* **109**, 417 (1984).
- ¹⁷MOLECULE is a Gaussian integral program written by J. Almlöf.
- ¹⁸SWEDEN contains a vectorized SCF-MCSCF-direct CI program, as well as a conventional CI code that has been extended to do CPF and MCPF, written by P. E. M. Siegbahn, C. W. Bauschlicher, Jr., B. Roos, P. R. Taylor, A. Heiberg, J. Almlöf, S. R. Langhoff, and D. P. Chong.